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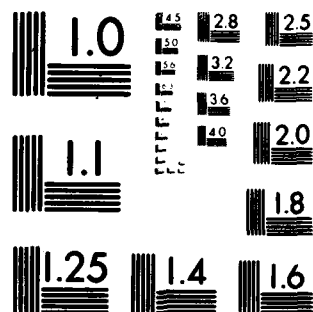
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Cofacially Linked Metallomacrocyclic Conductive Polymers. Halogen
Dopant Level and Macromolecule Architecture, Electronic Structure,
and Charge Transport

by

B. N. Diel, T. Inabe, J. W. Lyding, K. F. Schoch, Jr.,
C. R. Kannewurf, and T. J. Marks

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This paper presents an integrated study of the nature of the halogen doping process for the cofacially joined electrically conductive metallomacrocyclic polymers $[M(Pc)O]_n$, M=Si,Ge,Sn; Pc=phthalocyaninato. The properties of the $\{[M(Pc)O]Br_y\}_n$ and $\{[M(Pc)O]I_y\}_n$ materials have been studied in detail as a function of y by X-ray diffractometry, infrared, optical, resonance Raman, EPR, four-probe van der Pauw, and static magnetic susceptibility. All data are in accord with a principally heterogeneous doping process. The sensitivity of the physical properties to M and interplanar (ring-ring) spacing is clearly evident.

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COFACIALLY LINKED METALLOMACROCYCLIC CONDUCTIVE POLYMERS.
HALOGEN DOPANT LEVEL AND MACROMOLECULE ARCHITECTURE,
ELECTRONIC STRUCTURE, AND CHARGE TRANSPORT
BY
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INTRODUCTION

The face-to-face assembly approach represents a new and highly successful strategy for controlling molecular stacking and lattice architecture in low-dimensional mixed valence materials (1-5). As illustrated in eq.(1), it

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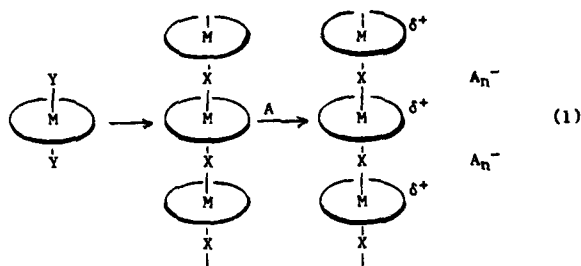
offers the possibility of constructing an almost infinite variety of conductive macromolecules, composed of well-characterized metallomacrocyclic subunits and having well-defined primary and secondary structures. For the phthalocyanine systems where M=Si,Ge,Sn, and X=O, we have shown that halogen doping (A = $1/2I_2, 1/2Br_2$) results in conductive, ligand-oxidized polymers in which the facility of charge transport reflects the influence of M on the ring-ring interplanar spacing (1-5). Furthermore, the inviolability of the stacking allows an incisive probing of the donor-acceptor relationships which is impossible in simple molecular systems (4,5). Much still remains to be learned, however, about the halogen partial oxidation process, especially as regards the response of the polymer molecular and electronic structure as well as charge transport to dopant introduction. Unresolved issues such as the homogeneity of the doping process are of fundamental importance in understanding the properties of all electrically conductive organic polymers (6). In this contribution, we address these problems in the $\{[M(Pc)O]X_y\}_n$ series of materials (M = Si,Ge,Sn; X = Br,I) through a systematic study of selected physicochemical properties as a function of dopant level.

EXPERIMENTAL

The face-to-face polymers were prepared as described elsewhere (2,4,7). Infrared, Raman, EPR, and four-probe conductivity measurements were performed as previously described (4,7). X-ray powder diffractometry was performed with a Rigaku Geigerflex diffractometer using filtered CuK$_\alpha$ radiation. Magnetic susceptibility measurements were made with a SHE VTS-10 SQUID Susceptometer.

RESULTS AND DISCUSSION

Properties of the Undoped $[M(Pc)O]_n$ Materials. As discussed elsewhere (2,4,7), spectroscopic and X-ray diffraction (powder and single crystal of model compounds) are consistent with the cofacially linked macromolecular structure shown in eq.(1). Derived interplanar spacings (metal-metal distances) are 3.32(2)Å (M=Si), 3.55(2)Å (M=Ge), and 3.84(2)Å (M=Sn). As a comparison, the analogous spacing in the "molecular metal" $[Ni(PcO]I_{1.0}$ is 3.244(2)Å (8). End group analysis by FT-IR spectroscopy yields average degrees of polymerization of n $\geqslant$ 120 (M = Si), n $\geqslant$ 60 (M = Ge), and n $\geqslant$ 115 (M = Sn) (4,5,7).

Doping and Degree of Partial Oxidation. The M=Si,Ge,Sn polymers were incrementally doped with iodine and the state of iodine monitored by resonance Raman spectroscopy (1,9).

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From y$\cong$0.1 up to y$\cong$1, the only detectable polyiodide was I_3^-. Above this point, increasing amounts of I_5^- were detectable. The M=Si compound was also examined for X=Br; the Br_3^- ion was the only species detected up to y $\cong$ 1.8. These results indicate that for low to moderate doping levels, the formal oxidation states of the face-to-face linked phthalocyanines can be represented as $\{[M(Pc)^{+y/3}O]-(X_3^-)_{y/3}\}_n$. That the partial oxidation involves orbitals which are predominantly ligand in character is confirmed by EPR and transmission optical spectroscopy. For the former, spin Hamiltonian parameters are typical of organic π cation radicals (g $\approx$ 2.003) (4,7), while the latter show a red shift of the π-π^* transitions typical of phthalocyanine radical cations (7).

Solid state infrared transmission spectra of the polymers exhibit, upon incremental doping, the growth of electronic absorption typical of mixed valence molecular and macromolecular metals (7,10). Representative data are shown in Figure 1. The effect is qualitatively stronger for the silicon polymer than for the other polymers, presumably reflecting the greater ring-ring overlap.

Doping and Charge Transport. As shown in Figure 2, progressive iodine doping of the silicon and germanium polymers results in a rapid rise in conductivity, followed by a leveling off. In other conductive polymers, such a response has been explained in terms of a classical insulator (or semiconductor)-to-metal transition (12) as well as by percolation through a heterogeneous medium containing both conductive and nonconductive particles (6). In the present case, it should be noted that the powder conductivity of the highly doped $\{[Si(Pc)O]I_y\}_n$ materials is comparable to that of $[Ni(Pc)]I_{1.0}$ powders. The conductivity of the $\{[Ge(Pc)O]I_y\}_n$ materials is significantly lower, in accord with the increased interplanar separation. The interplanar spacing in the $\{[Sn(Pc)O]I_y\}_n$ polymers is even greater, and the conductivities are lower by several additional orders of magnitude. The interpretation of powder conductivities is complicated by the fact that transport is sampled over all crystallographic directions and includes interparticle contact resistance. A qualitative sampling of the conductivity in the $\{[M(Pc)O]^{+y/3}\}_n$ chain direction can be obtained from voltage-shorted compaction measurements (5,7). In the case of M=Si, the transport is "metal-like" ($d\sigma/dt < 0$) down to 100°K.

The temperature dependence of the $\{[M(Pc)O]I_y\}_n$ conductivity was also investigated as a function of dopant level. The conductivities are thermally activated as is typically found for powder measurements. The effect of increasing dopant level is to lower the apparent activation energy for the conduction process. Similar behavior is observed in doping studies of polyacetylene (12).

Doping and Polymer Lattice Architecture. The $\{[M(Pc)O]I_y\}_n$, M=Si,Ge, and $\{[Si(Pc)O]Br_y\}_n$ materials were investigated by X-ray powder diffractometry to obtain information on two important points: i) the structures of the halogen doped face-to-face polymers; ii) whether the doping process is homogeneous. The $\{[Si(Pc)O]I_y\}_n$ and $\{[Ge(Pc)O]I_y\}_n$, y $\approx$?. ..der patterns are remarkably similar to that of Ni' The latter material has a tetragonal crystal struc ' .tacks of staggered Ni(Pc)$^{+0.33}$ units and chains o. I$_3$. terions extending parallel to c (8). The similarity of the doped face-to-face polymer powder patterns suggests a similar crystal structure. The polymer powder patterns can be indexed in the tetragonal crystal system, and lattice parameters obtained via an iterative computer fit are set out in Table I. The measured densities of the doped polymer pellets are in agreement with those calculated assuming a $Ni(Pc)I_{1.0}$-like structure.

A major issue for all doped conductive organic polymers concerns whether the dopants distributed uniformly throughout the polymer matrix (the classic picture of doping) or whether only discrete phases of narrow donor:acceptor stoichiometry exist. Thus, the $\{[M(Pc)O]I_y\}_n$, M=Si and Ge, and $\{[Si(Pc)O]Br_y\}_n$ materials were subjected to a detailed diffractometric investigation as a function of doping for y=0 to ca. 1. As illustrated for M=Ge in Figure 3 and found for all of the materials, as halogenation progresses, the $[M(Pc)O]_n$ phase disappears, and a new phase having the

$Ni(Pc)I_{1.0}$-like structure grows in. At intermediate stages of doping, the diffraction patterns can be duplicated by simple admixture of the y=0 and y ≈ 1 phases. Clearly the halogen doping of the $[M(Pc)O]_n$ polymers is predominantly if not exclusively heterogeneous.

Doping and Polymer Magnetism. For $[Si(Pc)O]_n$ and $[Ge(Pc)O]_n$, a detailed study of magnetic susceptibility was conducted as a function of iodine dopant level from 2-300°K. After subtraction of "Curie tailing" due to impurities, the paramagnetic component of the $\{[Si(Pc)O]I_y\}_n$ susceptibility is Pauli-like (as found for $Ni(Pc)I_{1.0}$ (8)). The magnitude of the Pauli susceptibility increases linearly with y, consistent with the aforementioned evidence for the heterogeneity of the doping, i.e., a single phase with $\chi_p \approx 210 \times 10^{-6}$ emu/mol is being produced. For the doped germanium materials, the paramagnetism of the non-Curie part of the spin susceptibility is slightly larger, and exhibits weak antiferromagnetic temperature dependence, consistent with diminished ring-ring overlap. Again, the strength of this paramagnetism is almost linearly dependent upon the doping level.

CONCLUSIONS

This study underscores the viability of the cofacial assembly approach when coupled with partial oxidation for the synthesis of new, electrically conductive macromolecules. Robust, "tailored" materials having transport properties ranging from "metal-like" to semiconducting are readily accessible. In regard to the partial oxidation process, the present study also demonstrates that the halogen doping is unambiguously heterogeneous.

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Table I. Unit Cell Parameters of Iodine-Doped Phthalocyanine Materials

	$Ni(Pc)I_{1.0}$[a]	$\{[Si(Pc)O]I_{1.13}\}_n$	$\{[Ge(Pc)O]I_{1.12}\}_n$
a(Å)	13.936(g)[a]	13.92(2)	13.96(2)
c(Å)	6.488(3)[a]	6.60(2)	6.96(2)
ρ_{calcd}(g/cm³)	1.84	1.80	1.82
ρ_{obs}(g/cm³)	1.78(4)[a]	1.60(16)	1.66(17)

[a]Single crystal data
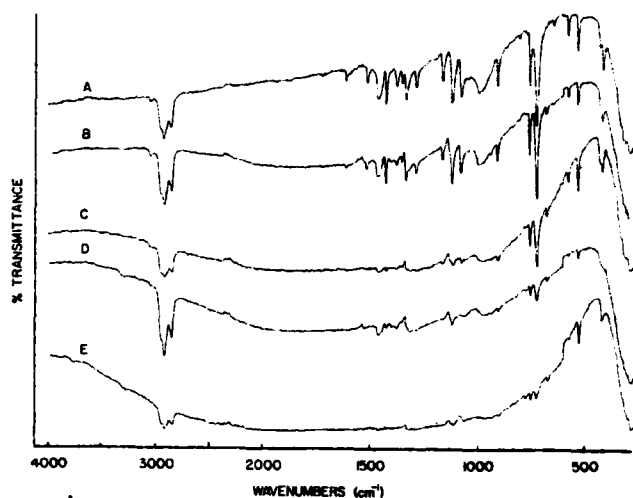

Fig. 1. Infrared spectra of $\{[Si(Pc)O]I_y\}_n$ for A. y=0.00; B. y=0.12; C. y=0.31; D. y=0.71; E. y=1.13. Recorded as Nujol mulls between KBr plates.
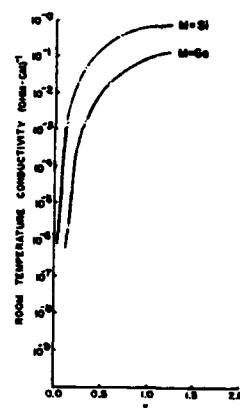

Fig. 2. Pressed powder conductivity for $\{[M(Pc)O]I_y\}_n$ materials as a function of dopant concentration.
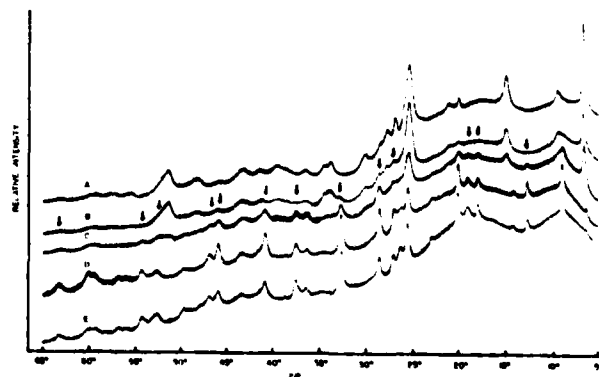

Fig. 3. X-ray powder diffraction patterns of $\{[Ge(Pc)O]I_y\}_n$ for A. y=0.00; B. y=0.14; C. y=0.31; D. y=1.07; E. y=1.12. Arrows denote reflections of the doped phase

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